Alkaline magmatism in the Paraná Basin: A comparative study. II. Geochronology and geochemistry

Magmatismo alcalino na Bacia do Paraná: Um estudo comparativo. II. Geocronologia e geoquímica

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ABSTRACT
Radiometric data demonstrate the age variability of alkaline magmatic events that affected the Paraná Basin. The oldest event, dated to the Middle Triassic (241 Ma), took place in border areas between Brazil and Paraguay. Four distinct episodes are distinguished in the Early Cretaceous. The earliest of these (139 Ma) predates the emplacement of the tholeiitic lava flows of the Serra Geral group. It is followed by a post-tholeiitic episode (126 Ma) containing the largest number of alkaline occurrences in Eastern Paraguay. A late Early Cretaceous event (118 Ma) is exclusive to the southeastern portion of the territory. A brief episode (110-100Ma) is associated to the Ponta Grossa arch. The Late Cretaceous episode (90–70 Ma), not recorded in Paraguay, is compositionally diverse and particularly widespread in Brazilian areas of the basin, with a minor occurrence in Bolivia (Candelaria). Paleogene alkaline rocks primarily forming small dikes and plugs (59 Ma) represent the youngest alkaline expressions, found in both Brazilian and Paraguayan domains. The alkaline magmatism ranges in composition from ultrabasic to acid, prevailing evolved intrusive silica-undersaturated to silica-saturated types of potassic nature and variable K/Na ratios. The geochemical characteristics of the associated petrographic assemblages are described for each alkaline province, and general considerations are presented regarding the genesis of the alkaline magmatism.
Keywords: Alkaline magmatism; Paraná Basin; Brazilian Platform; Alkaline Province

RESUMO
Idades radiométricas evidenciam a variabilidade da idade dos eventos magmáticos alcalinos que afetaram a Bacia do Paraná. O primeiro, datado do Triássico Médio (241 Ma), ocorreu em áreas da borda do Brasil e Paraguai. Quatro episódios são distinguidos no Cretáceo Inferior. O mais antigo deles (139 Ma) precede a colocação das lavas toleiíticas do grupo Serra Geral. Ele é seguido por um episódio pós-toleiítico (126 Ma) contendo o maior número de ocorrências alcalinas do Paraguai Oriental. Um evento tardio do Cretáceo Inferior (118 Ma) é exclusivo da sua porção sul-oriental. Um breve episódio (110 - 100 Ma) é associado com o arco Ponta Grossa. O evento do Cretáceo Superior (90-70 Ma), não reconhecido no Paraguai, é composicionalmente variável e se mostra muito difundido em território brasileiro, além de uma pequena ocorrência na Bolívia (Candelaria). Rochas alcalinas do Paleogeno, formando diques e plugs (59 Ma), representam a expressão mais nova do magmatismo, sendo encontrada em domínios brasileiro e paraguaio. O magmatismo alcalino tem composição modificável de ultrabásica a ácida, predominando os tipos intrusivos evoluídos insaturados a saturados em sílica de natureza potássica e razões K/Na distintas. As características geoquímicas das associações petrográficas são descritas para cada província alcalina, e considerações gerais são apresentadas sobre a gênese do magmatismo alcalino.
Palavras-chave: Magmatismo alcalino, Bacia do Paraná, Plataforma Brasileira, Província alcalina

DOI:10.21715/GB2358-2812.202539004

1 INTRODUCTION

Alkaline magmatism is an important geological element in the evolution of the southern Brazilian Platform, and its different aspects have been the subject of extensive investigation over the past years, as exemplified by volumes such as those of COMIN-CHIARAMONTI and GOMES (1996, 2005), GOMES and COMIN-CHIARAMONTI (2017), and GOMES (2020, 2023), as well as numerous review articles, particularly addressing analytical data on rocks and minerals. Records of this alkaline magmatism are more abundant in two South American countries, Brazil and Paraguay, and are tectonically controlled by crustal discontinuities (arches, rifts, lineaments, and faults), mainly bordering the Paraná, Pelotas, and Santos sedimentary basins. A large variety of igneous forms is present, with intrusive rocks prevailing over hypabyssal and extrusive types. The sizes, compositions, and ages of the intrusions are also varied. The largest occurrence is represented by the Poços de Caldas massif in Brazil, which extends over 800 km². Considering aspects such as geological setting, petrographic data, and radiometric ages, the numerous centers of alkaline magmatism were grouped into distinct, isolated occurrences referred to as *alkaline provinces* by ALMEIDA (1971). These alkaline clusters frequently follow a linear pattern which is parallel to the coast and the erosive margin of the Paraná Basin over a considerable area. The initial number of 12 alkaline provinces proposed by ALMEIDA (1971) was later increased to 15 by RICCOMINI *et al.* (2005) and to 16 following the recommendations of GASPAR *et al.* (2003). Figure 1 shows the distinct alkaline provinces and the main tectonic features associated with the Paraná sedimentary basin.

- Alto Paraguay (Brazil-Paraguay);
- Rio Apa, Amambay, Central, Asunción and Misiones (Paraguay);
- Velasco and Candelaria (Bolivia);
- Valle Chico (Uruguay) and Piratini;
- Rondonópolis Anteclise;
- Ponta Grossa Arch, Serra do Mar, Cabo Frio Magmatic Lineament, Alto Paranaíba, and Goiás.

2 GEOCHRONOLOGY

Investigation of radiometric ages for alkaline rocks in the Paraná Basin began with the establishment of the Geochronology Laboratory at the University of São Paulo in the early 1960s, when two research projects were initiated to determine K-Ar ages, one focused on the flood basalts overlying rocks of the Paraná Basin (AMARAL *et al*., 1966) and the other one on the alkaline rocks in Southern Brazil (AMARAL *et al*., 1967). The second project involved the collection of samples from several alkaline occurrences in Brazil and Eastern Paraguay. Using the updated decay constants of STEIGER and JÄGER (1977), the recalculation of analytical data by SONOKY and GARDA (1988) revealed a wide age span for the alkaline events, with clearly distinct groups identified in the cumulative histogram (ULBRICH; GOMES 1981). In the following years additional methods such as Rb/Sr, U/Pb, Sm/Nd, Ar/Ar, and more recently, U/Pb on perovskite, were employed in dating programs. The overall results confirmed previously identified activity peaks and indicated an age span of approximately 200 Ma for the entire set of events. Magmatism ranges in age from Mesozoic to the Paleogene with pulses of alkaline activity occurring in the Middle Triassic and, especially, during the Cretaceous. In general terms, data also provide evidence that the ages of alkaline magmatism tend to decrease from western to eastern margins of the Paraná Basin, as previously observed by ULRICH and GOMES (1981).

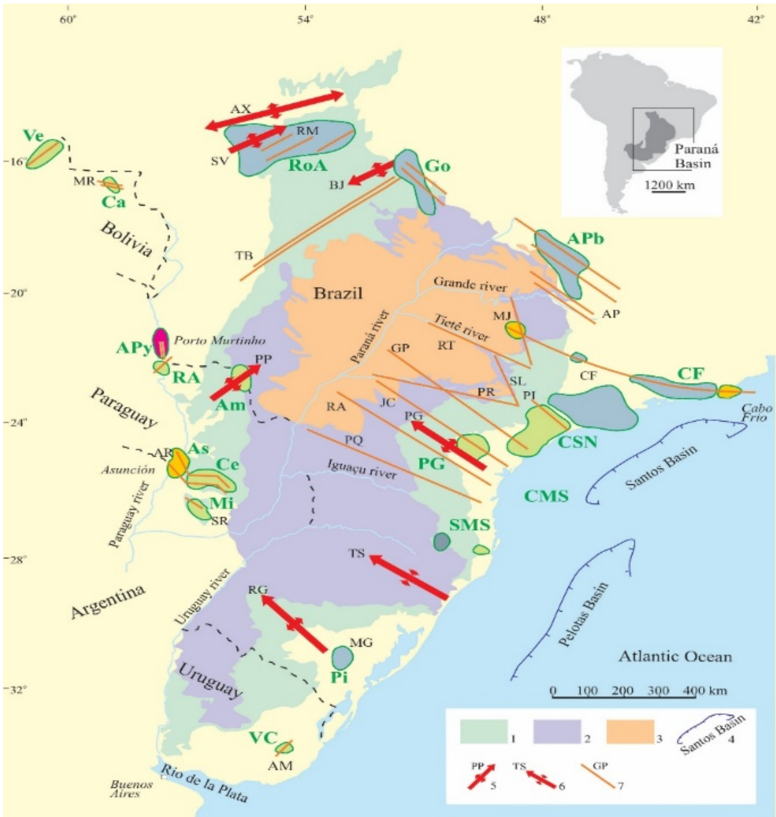

Figure 1. Geographic distribution of alkaline magmatism events affecting the Paraná Basin (after RICCOMINI *et al.,* 2005, modified). **Legends:** 1, Late Ordovician to Early Cretaceous Paraná Basin; 2, Early Cretaceous tholeiitic lava flows; 3, Late Cretaceous Bauru Basin; 4, Offshore marginal basins; 5, Axes of main arches (AX – Alto Xingu; SV – São Vicente; BJ – Bom Jardim de Goiás; PG – Ponta Grossa; RG – Rio Grande; PP – Ponta Porã); 6) Torres Syncline; 7) Major fracture zones, in part deep lithospheric faults (Rifts: MR – Mercedes; RM – Rio das Mortes; MG – Moirão; SR – Santa Rosa; AR – Asunción. Lineaments: TB – Transbrasiliano; AP – Alto Paranaíba; MJ – Moji Guaçu; CF – Cabo Frio; RT – Rio Tietê; SL – São Carlos–Leme; PR – Paranapanema; PI – Piedade; GP – Guapiara; JC – São Jerônimo–Curiúva; RA – Rio Alonzo; PQ – Rio Piqueri; AM – Santa Lúcia–Aiguá–Merín). **Alkaline field ages:** Middle Triassic, pink; Early Cretaceous, light green; Late Cretcaous, blue; Paleogene, yellow.

2.1 MIDDLE TRIASSIC MAGMATISM

The oldest known alkaline magmatism event to affect the Paraná Basin is restricted to the Alto Paraguay province, in the border region between Brazil and Paraguay, and it has been thoroughly investigated over the years using various analytical techniques. K/Ar ages from mineral concentrates (alkali feldspar and biotite) were first reported by AMARAL *et al.* (1967) for nepheline syenites from the Pão de Açúcar complex, suggesting an age of 238 Ma for the occurrence. Shortly after, COMTE and HASUI (1971) provided an age of 209 Ma for a phonolite sample from the same intrusion. Additional information came from the work by GOMES et al. (1996a), bearing a K/Ar cumulative histogram with 250–240 Ma as the most abundant class interval for the analyses, and from systematic research performed by VELÁZQUEZ (1996) and VELÁZQUEZ *et al.* (1966a, b) on various complexes utilizing K/Ar and Rb/Sr methods. Rb/Sr isochrones for Cerro Boggiani, Fecho dos Morros, Pão de Açúcar, and Cerro Siete Cabezas provided by these authors yielded ages of 250.9 ± 2.1 Ma and 255.0 ± 11.0 Ma. Sm/Nd isochrones for agpaitic and miaskitic suites by COMIN-CHIARAMONTI *et al.* (2015) yielded values of 254 ± 31 Ma and 259 ± 53 Ma, respectively. Ages for the entire set of recorded data, obtained through various techniques (K/Ar, Rb/Sr, and Sm/Nd), are highly variable. Velázquez et al. (1996b) and

COMIN-CHIARAMONTI *et al.* (2015) argue that this variability is apparently due to mineral disequilibrium caused by subsolidus reactions, exsolution, mineral zoning, and chemical changes resulting from hydrothermal alteration and weathering, which affected the behavior of minerals such as alkali feldspar and amphiboles. Taking into account these sources of uncertainty, several highly reliable Ar/Ar analyses were conducted on mineral separates (alkali feldspar, plagioclase, amphibole, and biotite) and whole-rock samples from various alkaline occurrences at the University of California (UC Berkeley) and the University of São Paulo (USP, São Paulo). A total of 33 selected analyses of biotite concentrates (K_2O = 9–10.5%) from Paraguayan alkaline rocks was reported by COMIN-CHIARAMONTI *et al.* (2007c), including three analyses from the Alto Paraguay province (Cerro Boggiani, Cerro Siete Cabezas, and Stock I), performed at UC Berkeley laboratories. Two additional analyses on specimens from Pão de Açúcar and Cerro Pedreira, conducted at USP laboratories in São Paulo, are presented by COMIN-CHIARAMONTI *et al.* (2015). The total recorded plateau data and integrated measurements from the five analyses range from 240.6 ± 0.4 Ma to 242.2 ± 0.9 Ma, with an average of 241.8 ± 1.1 Ma (Figure 2), the preferred age for the province.

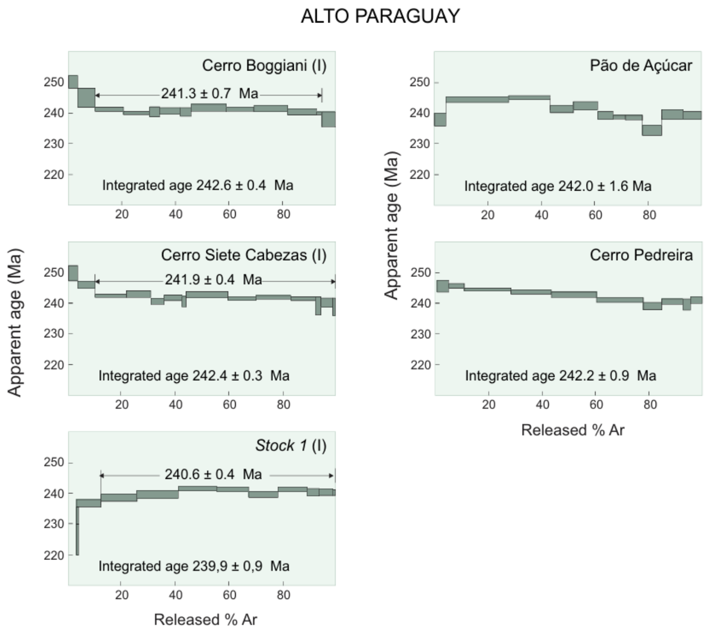

Figure 2. Ar/Ar spectra for biotite from alkaline occurrences in the Alto Paraguay province: Cerro Boggiani, Cerro Siete Cabezas, and Stock I (after COMIN-CHIARAMONTI *et al.*, 2007c); Cerro Pão de Açúcar and Cerro Pedreira (after COMIN-CHIARAMONTI *et al.*, 2015).

2.2 EARLY CRETACEOUS MAGMATISM

The Early Cretaceous alkaline events that affected primarily the Paraná Basin are marked by a highly variable magmatic activity, represented by distinct and recurrent pulses spanning approximately 30 million years in southern portions of the Brazilian Platform.

2.2.1 THE 139 Ma EPISODE

The event, predating the flood tholeiitic lavas of the Serra Geral group, is found in the western border of the Paraná Basin and confined to the Paraguayan and Bolivian domains. In the first country, the rocks are linked to the Rio Apa and Amambay provinces, while in the second, to the Velasco province. In both situations, the geochronologic documentation is very deficient, consisting of a few age determinations.

Small basanite dikes occurring in the Valle-mí area, northern Paraguay, were analyzed by GIBSON *et al.* (1995) using the K/Ar method on whole-rock samples. The results indicate an age of 142 ± 2 Ma, closely matching subsequent K/Ar values reported by CASTORINA *et al.* (1997) 137 ± 7 Ma and 138 ± 9 Ma for a phonotephrite dike—as well as an Ar/Ar plateau age of 138.7 ± 0.2 Ma from COMIN-CHIARAMONTI *et al.* (2007c). These data suggest that the Rio Apa alkaline magmatism is Early Cretaceous in age and associated with the 139 Ma pulse.

The second event of similar age in Paraguay is recorded in the northeastern part of the country, associated with the Amambay province. The magmatism encompasses several intrusions, including two carbonatite complexes, Cerro Chiriguelo and Cerro Sarambí. Radiometric data spans a wide range of ages, including determinations by fission track on apatite and titanite (EBY and MARIANO, 1986, 1992), K/Ar (COMTE and HASUI, 1971), and Ar/Ar methods (GIBSON *et al*., 2006; COMIN-CHIARAMONTI *et al.,* 2007c). Data presented by GIBSON *et al.* (2006) for phlogopite specimens from the Arroyo Gasory trachyte and the Cerro Sarambí lamprophyre point to ages of 144.99 Ma and 144.95-144.96 Ma for the first and the second intrusions, respectively. Ar/Ar analyses of biotite separate from glimmeritic veins related to the Cerro Sarambí carbonatite and from a trachytic lava flow interbedded with the Cerro Chiriguelo carbonatite are reported by COMIN-CHIARAMONTI *et al.* (2007c), yielding ages of 139.6 ± 0.2 Ma and 137.9 ± 0.3 Ma, respectively, with an average of 138.0 ± 1.6 Ma. This Early Cretaceous alkaline magmatism is clearly pre-tholeiitic, as confirmed by field evidence showing basalts overlying the alkaline rocks (GOMES *et al.,* 2011a).

Alkaline rocks that occur in Velasco, southeastern Bolivia, are related to the 139 Ma magmatic episode. Most geochronological studies on these rocks were conducted in the 1970s by a British mission that carried out extensive fieldwork in the area. DARBYSHIRE and FLETCHER (1979) registered K/Ar analyses of biotite and amphibole separates, with ages within the 142-134 Ma interval and mean values of 138 ± 5 Ma and 136 ± 5 Ma for quartz-syenites and syenites, respectively. Rb/Sr isochrones provided concordant ages, with values of 143 ± 4 Ma for syenitic and granitic rocks from the Cerro Cabeza de Toro pluton and of 140 ± 6 Ma for silica-undersaturated varieties from the Cerro Bamba intrusion. Dikes of nepheline syenite correspond to ages of 138 ± 4 Ma. An Ar/Ar age of 138.1 ± 0.3 Ma was reported more recently by GOMES *et al.* (2008).

2.2.2 THE 130-126 Ma EPISODE

An age pulse of approximately 130 Ma characterizes the Valle Chico province in Uruguay (RUBERTI *et al*., 2005, formerly the Mariscala province, cf. ALMEIDA, 1971), magmatic records in central-eastern Paraguay, and some occurrences linked to the Ponta Grossa Arch province in Brazil. Intrusive syenites and granites, along with their fine-grained equivalents from the Valle Chico massif—associated with basaltic and acidic volcanic rocks—were dated by UMPIERRE and HALPERN (1971) and BOSSI and UMPIERRE (1975) using the Rb/Sr technique, yielding ages of 124 ± 5 Ma and 123 ± 3 Ma, respectively. STEWART *et al.* (1996) reported an Ar/Ar age of 132 ± 2 Ma for a syenitic sample, while PIRELLI (1999) obtained an age of 138 ± 8 Ma based on amphibole concentrate and bulk-rock analysis. Meanwhile, MUZIO *et al.* (1999) determined a U/Pb age of 128.2 ± 0.2 Ma on zircon crystals. A comparable age of 128.1 ± 1.6–1.7 Ma was proposed for the massif by LUSTRINO *et al.* (2005), employing the same methodology and using zircon populations extracted from syenitic and volcanic rocks. For the associated basic and acidic volcanic rocks, KIRSTEIN *et al.* (2000) reported Ar/Ar ages ranging from 134 to 130 Ma for the former, while STEWART *et al.* (1996) and KIRSTEIN (1997) recorded values between 132 and 124 Ma for the latter.

The Ponta Grossa arch region is characterized by intense Cretaceous magmatic activity, encompassing both Paraná tholeiitic basalts and alkaline rocks. The former is represented by hundreds of NW-trending dikes and important magnetic alignments, which have been extensively studied in recent years. The latter corresponds to alkaline events, including two from the Early Cretaceous and one from the Late Cretaceous. The oldest of the Early Cretaceous alkaline magmatic episodes, believed to be contemporaneous with the flood basalts of the Paraná large igneous province (~130 Ma; THIEDE; VASCONCELOS, 2010; JANASI *et al*., 2011), intrudes the Neoproterozoic basement and is geographically associated with the São Jerônimo–Curiúva (Barra do Itapirapuã), Guapiara (Jacupiranga, José Fernandes, Juquiá), and Piedade (Ipanema, Itanhaém, Piedade) lineaments. Anitápolis, to the south, appears to be unaffected by these structures. With few exceptions, K/Ar determinations for the Ponta Grossa occurrences are scarce and mostly fall within the 140–120 Ma interval (Figure 3). A recent investigation of the Piedade carbonatite by RUBERTI *et al.* (2024) yielded an Ar/Ar age of 133.0 ± 0.2 Ma, confirming the Early Cretaceous age of the complex.

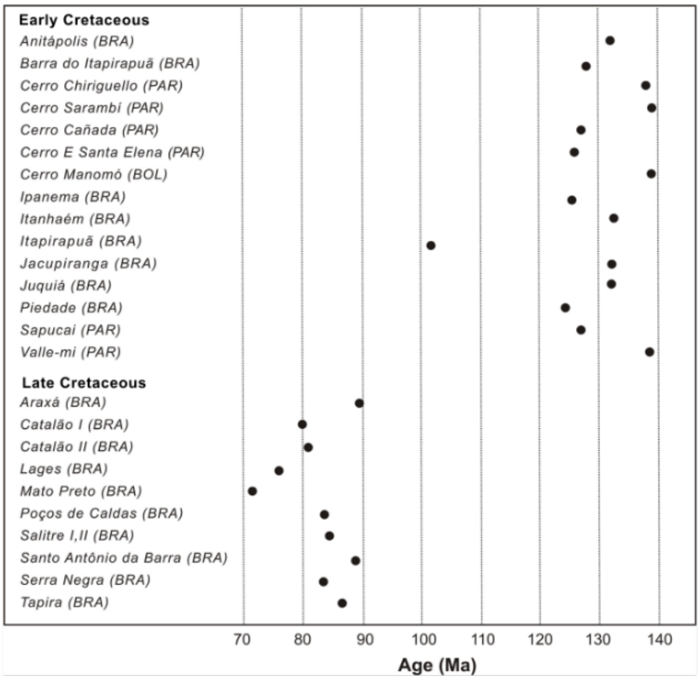

Figure 3. Radiometric ages of individual alkaline intrusions within the Ponta Grossa arch domain, determined by various geochronological methods (after GOMES *et al.,* 2011b, modified).

Central-eastern Paraguay is the site of numerous alkaline intrusions along the Asunción-Sapucai-Villarrica rift. K/Ar ages in the Sapucai district, the largest known alkaline occurrence in the area, were obtained by COMTE and HASUI (1971), PALMIERI and ARRIBAS (1975) and VELÁZQUEZ *et al.* (1992) employing the method. However, the low reliability of many results, which display variations as wide as 40 Ma, raised concern about the suitability of the method. Ar/Ar ages were thus introduced, with the study by MILAN (2003) being the first source of Ar/Ar ages for the alkaline magmatism in the area. Radiometric dates from biotite and plagioclase separates and bulk-rock samples, as determined by the aforementioned author, were subsequently plotted by GOMES *et al.* (2003) in cumulative age histograms, revealing a unimodal distribution in the 128–126 Ma range. These values are consistent with the Rb/Sr isochrones of 128 ± 8 Ma and 127.8 ± 7.2 Ma reported by BITSCHENE (1987) and VELÁZQUEZ *et al.* (1992), respectively. COMIN-CHIARAMONTI *et al.* (2007c) provided additional Ar/Ar plateau ages (Figure 4) for rocks from several intrusions, with an average value of 126.4 ± 0.4 Ma. Similar values were recorded by GIBSON *et al*. (2006) for biotite concentrates from the Cerro Santo Tomás dike (127.91 ± 0.79 Ma and 127.66 ± 0.79 Ma) and from the stock of Cerro Cañada (127.12 ± 0.78 Ma). Numerous dating (K/Ar, Ar/Ar and Rb/Sr) are available for rocks of central Paraguay, primarily listed in the papers by

VELÁZQUEZ *et al.* (1992), GOMES *et al.* (1996a), COMIN-CHIARAMONTI *et al.* (1996, 2007b, c), MILAN (2003), and in GOMES and COMIN-CHIARAMONTI's (2017) volume.

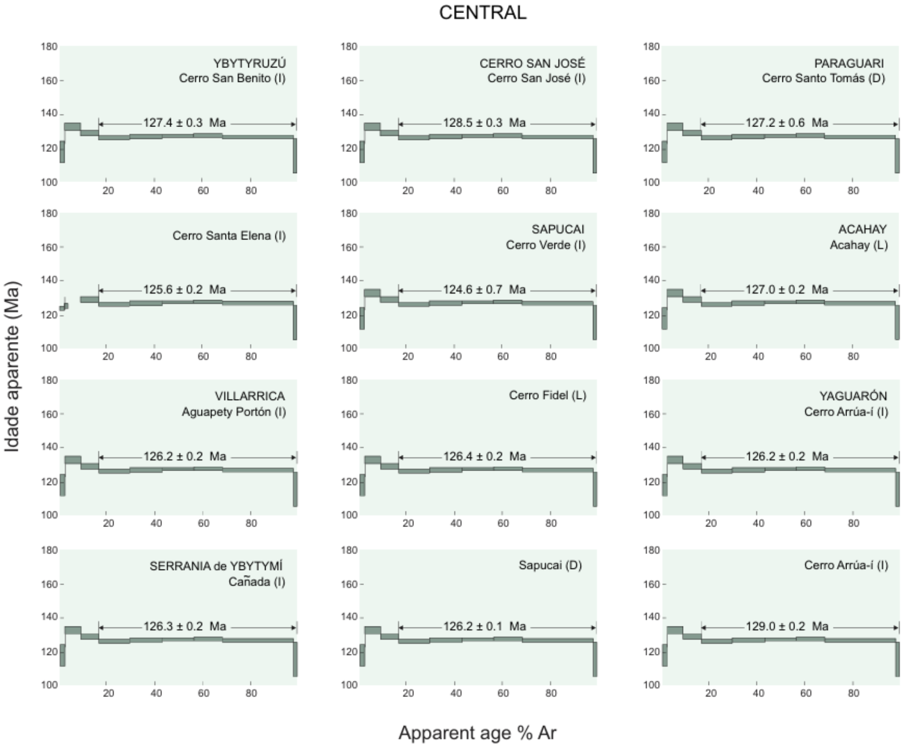

Figure 4. Ar/Ar spectra for bulk rock samples (Cerro Acahay and Cerro Arrúa-í) and biotite separates from alkaline intrusions in the Central province, Eastern Paraguay (after MILAN, 2003; COMIN-CHIARAMONTI *et al.*, 2007c).

2.2.3 THE 118 Ma EPISODE

This event is represented by a few outcrops of sodic alkaline rocks located near San Juan Bautista and San Ignacio in southeastern Paraguay. Age data for these rocks are provided by VELÁZQUEZ *et al.* (2006) and COMIN-CHIARAMONTI *et al.* (2007c), based on Ar/Ar spectra obtained from three small plugs of nephelinites/ankaratrites containing mantle xenoliths and from one peralkaline phonolite dike. The ages range from 117.9 ± 0.2 Ma to 119.8 ± 0.5 Ma, with a mean value of 118.3 ± 1.6 Ma. It is worth noting that this average value approximately corresponds to the youngest ages recorded for alkaline dikes in Florianópolis (119 Ma, RAPOSO *et al.,* 1998) and Ponta Grossa (120 Ma; RENNE *et al*., 1996), as well as for tholeiitic bodies along the southern Brazilian coast.

2.2.4 THE 110-100 Ma EPISODE

This brief alkaline event, which occurred within the domains of the Ponta Grossa arch, is represented solely by the Banhadão and Itapirapuã complexes in the Ribeira Valley. The former event appears to be devoid of carbonatites, whereas the latter exhibits small carbonatite veins cutting through nepheline syenites. Ar/Ar geochronological studies confirm the Early Cretaceous K/Ar ages previously reported for both complexes: Banhadão (phlogopite, 108.7 ± 2.1 Ma and 107.7 ± 3.1 Ma, with an average of 108.2 Ma; cf. RUBERTI, 1984; SONOKI; GARDA, 1988) and Itapirapuã (biotite, 104.8 and 101.4 Ma, with a mean age of 103.7 ± 4.3 Ma; cf. GOMES and

CORDANI, 1965). Recent analytical results by GOMES *et al.* (2018b) on melteigitic and phonolitic samples from the Banhadão complex indicate ages ranging from 110 to 106 Ma, with a minimum of 106 Ma. Biotite analyses of two samples from Itapirapuã—a melteigite and an enclave within nepheline syenite—yield similar results of 101.94 ± 0.59 Ma and 101.98 ± 0.27 Ma, respectively. Combined, the results suggest an emplacement age of 101.96 ± 0.65 Ma for the intrusion. U/Pb data are also available for titanite from a melanite-bearing syenite outcrop in Itapirapuã. Ages derived from Pb/U age diagrams and Pb/Pb - U/Pb isotopic ratios correspond to 105.0 ± 2.5 Ma and 106.8 ± 3.7 Ma, respectively, suggesting an age of approximately 106 Ma for the complex.

2.3 LATE CRETACEOUS MAGMATISM

The Late Cretaceous alkaline magmatism primarily represented in central-eastern Brazil by the extensive massifs of Poços de Caldas, Itatiaia and Passa Quatro was the most significant event of this nature to affect the Paraná Basin. The Serra do Mar, Cabo Frio Lineament, Alto Paranaíba, and Goiás provinces are other major areas containing coeval alkaline rocks. Other occurrences include Candelaria, Piratini, and the Rondonópolis Anteclise.

In southern areas of the basin, within the Sul-Riograndense shield, this alkaline magmatism is represented by the Piratini phonolitic suite, which is mainly composed of tephritic phonolites and subordinate peralkaline phonolites. These rocks were originally described by RIBEIRO (1971) and later investigated in detail by BARBIERI *et al.* (1987) and PHILIPP *et al.* (2005). K/Ar ages presented by BARBIERI *et al.* (1987) - recalculated by SONOKI and GARDA (1988) - mostly from bulk-rock samples cluster at 84.6 ± 6.7 Ma, a value similar to that reported for alkaline intrusions in the Serra do Mar province.

In northern portions of the basin, within Bolivian territory, this magmatism is scarce, represented by a few intrusive blocks of syenite and fine-grained rocks buried beneath alluvial sediments of the Pantanal basin. These rocks are included in the Candelaria province, with K–Ar ages reported by LITHERLAND *et al.* (1986) for the main types of present (nordmarkites, quartz syenites, and micronordmarkites). Ages are highly variable: 116 ± 7 Ma and 90 ± 3 Ma for hornblende concentrates and 76 ± 2 Ma for bulk-rock samples. A Late Cretaceous, post-Paraná basalt-lava genesis of the Candelaria province is confirmed by the Rb-Sr errorchron age of 79 ± 8 Ma, reported by COMIN-CHIARAMONTI *et al.* (2005b), and by Ar–Ar ages obtained by GOMES *et al.* (2008) on bulk-rock samples from the Cerro Los Angeles microsyenite and Cerro Pontudo trachyte. Integrated values were 86.18 ± 0.12 Ma and 86.14 ± 0.14 Ma, respectively.

Also, in northern areas of the basin, the magmatism of the Rondonópolis Anteclise is distinguished by two contrasting petrographic associations: the syenite-granite complex of Ponta do Morro and the volcanic rocks of the Poxoréu igneous province along the Rio das Mortes rift (GIBSON *et al.*, 1997). Geochronological documentation is extremely poor and inaccurate, with little data available in the literature. A Rb/Sr reference isochron for Ponta do Morro syenites yielded an age of 97.1 ± 1.1 Ma (SOUSA, 1997). Subsequently, however, the same author (SOUSA, 2013) reported a U/Pb (SHRIMP) value of 84.7 ± 0.59 Ma for the massif, similar to the Rb/Sr isochron formerly established by DEL'ARCO *et al.* (1982). Ar/Ar determinations for Poxoréu dikes correspond to an age of 83.4 ± 2.4 Ma (GIBSON *et al.*, 1995) and the 97-84 interval (SOUSA *et al.*, 2005). Associated kimberlites apparently belong to two distinct groups, as indicated by U/Pb ages: 94.6-91.6 Ma and 127.2-122.6 Ma (GREENWOOD et al. 1999; HEAMAN *et al.*, 1998).

Alkaline magmatism is widely distributed in the central-eastern Paraná Basin, cropping out on islands along the Serra do Mar range on the Atlantic coast of Brazil (Búzios, Monte de Trigo, São Sebastião, and Vitória) and in inland occurrences such as Bom Repouso and Ponte Nova in the Mantiqueira range, the Tunas and Cananeia massifs, as phonolitic plugs and dikes in the Ribeira Valley, and in the Lages complex southern Brazil. Data compiled from several sources indicates that the Neocretaceous alkaline episode is mainly confined to the 90-70 Ma interval. Ages from studies published prior to the compilation by SONOKI and GARDA (1988) clearly suggest a predominant modal class of 85–80 Ma for the Late Cretaceous occurrences. Recent high-precision Ar/Ar data on specimens from the island of São Sebastião reported by GIRALDO-ARROYAVE *et al.* (2021) point to a relatively narrow gap of 88-85 ± 0.6 Ma within the age interval of 90-80 Ma registered for other occurrences in southern Brazil, such as the intrusive rocks of the coastal islands (Búzios 81.3 ± 2.6 Ma, ALVES, 1997; Monte de Trigo 86.5 Ma, ENRICH *et al.*, 2006, 2009; Vitória 89.58 ± 3.18 Ma and 84.35 ± 3.92 Ma, MOTOKI *et al.*, 2018), Cananeia (83.6 Ma; SPINELLI and GOMES, 2008), Ponte Nova (87.6 ± 1.3 Ma, AZZONE *et al.*, 2009) and Tunas (84.7 ± 1.2 Ma; SIGA JR. *et al.*, 2007). Recent $^{40}Ar/^{39}Ar$ results by ROSA *et al.* (2024) on amphibole and biotite separates from phonolitic rocks in Bom Repouso yielded ages of 76.5 ± 0.4 Ma and 78.9 ± 0.4 Ma, respectively. In the Santos basin, lamprophyric dikes dated to approximately 82 Ma concentrate around the major syenitic massifs of Itatiaia, Passa Quatro and Morro Redondo and the Paleogene rift basins of Resende and Volta Redonda (GUEDES *et al.*, 2005). By the end of the Neocretaceous (~70 Ma), a younger pulse of alkaline magmatism is associated with the felsic alkaline stocks of the Serra do Mar province (Itatiaia; ROSA and RUBERTI, 2018; Passa Quatro; MONTES-LAUAR, 1998; BROTZU *et al.*, 1992) and dikes (GUEDES *et al.*, 2005).

2.4 PALEOGENE MAGMATISM

Paleogene magmatism is reported in Asunción and its vicinities, as represented by 15 bodies forming plugs, lava flows, and dikes of volcanic rocks (nephelinites/ankaratrites and subordinate peralkaline phonolites) bearing mantle nodules. Old K/Ar ages listed by COMTE and HASUI (1971), BITSCHENE (1987) and COMIN-CHIARAMONTI *et al.* (1991) for bulk-rock samples of these occurrences are highly variable. BITSCHENE (1987) lists a wide range of ages for the Cerro Confuso and Cerro Patiño intrusions, with values of 60.9 ± 4.4 Ma and 38.8 ± 2.3 Ma, respectively. A detailed investigation of magmatic records in Asunción was conducted by MILAN (2003) using the Ar/Ar method, with plateau and mini-plateau ages showing only minor variations. Plottings of these Ar/Ar data on a frequency histogram by GOMES *et al.* (2003) show the 58-56 Ma age interval as the dominant class. COMIN-CHIARAMONTI *et al.* (2007c), in turn, combined a subset of MILAN's (2003) results with new Ar/Ar datings and defined the 61–56 Ma interval as the range of variation. The latter authors also proposed an average value of 58.7 ± 2.4 Ma for the Asunción event. Figure 5 illustrates plateau and miniplateau ages for some volcanic rocks from Asunción. Isolated peralkaline phonolite plugs (e.g., Cerro Gimenez and Cerro Medina) located in the central region of the Asunción–Sapucai–Villarrica rift are possibly related to the Asunción magmatism, as suggested by the K–Ar age of 66.0 ± 4.6 Ma reported for the former (VELÁZQUEZ *et al.,* 1992).

Paleogene magmatism is also found in the Brazilian territory, mainly in central-eastern parts of the country. Manifestations are the ankaramitic lavas of the Volta Redonda and Itaboraí basins (RICCOMINI *et al.*, 1983, 1990; KLEIN; VALENÇA, 1984), the tinguaitic and analcimitic rocks from Jaboticabal and Aparecida do Monte Alto regions (GOMES; VALARELLI, 1970; COUTINHO *et al.*, 1982), the coastal dikes of southern Brazil (RAPOSO *et al.,* 1998) and, especially, several alkaline bodies linked to the Cabo Frio magmatic lineament. Data for the latter (Cabo Frio, Country Club, Itaúna, Mendanha, Monjolos, Morro de São João, Rio Bonito, Soarnho, Tangá) and dikes along the coast of São Paulo-Rio de Janeiro, are available in the literature (AMARAL *et al.*, 1967; SONOKI; GARDA. 1988; LIMA, 1976; CORDANI; TEIXEIRA, 1979; BROTZU *et al.*, 1989, 1997. 2005, 2007); SICHEL *et al.*, 1997; THOMPSON *et al.*, 1998; DECKART *et al.*, 1998; SMITH *et al.*, 1999; FERRARI, 2001; RICCOMINI *et al.,* 2005; GUEDES *et al.*, 2005; MOTOKI *et al.*, 2010, 2013; SILVA *et al.*, 2020), with all set of results including K/Ar, Ar/Ar and

Rb/Sr ages for mineral separates (amphibole, biotite, phlogopite and sanidine and bulk-rock samples presenting wide variation from 52.1 ± 0.8 Ma to 81.8 ± 1.8 Ma. So far, no critical analysis has been performed on these age determinations. Yet, many of them are probably imprecise. Tertiary values (lower or closer to 66.50 Ma) are consistent with Cabo Frio and other intrusions such as Rio Bonito (Ar/Ar and U/Pb ~65 Ma; SILVA *et al*., 2020) and Tanguá (Rb/Sr 66.8 Ma, MOTOKI *et al*., 2010) and coastal phonolitic dikes of the Santos basin (64.2 ± 1.9 Ma; GUEDES *et al*., 2005).

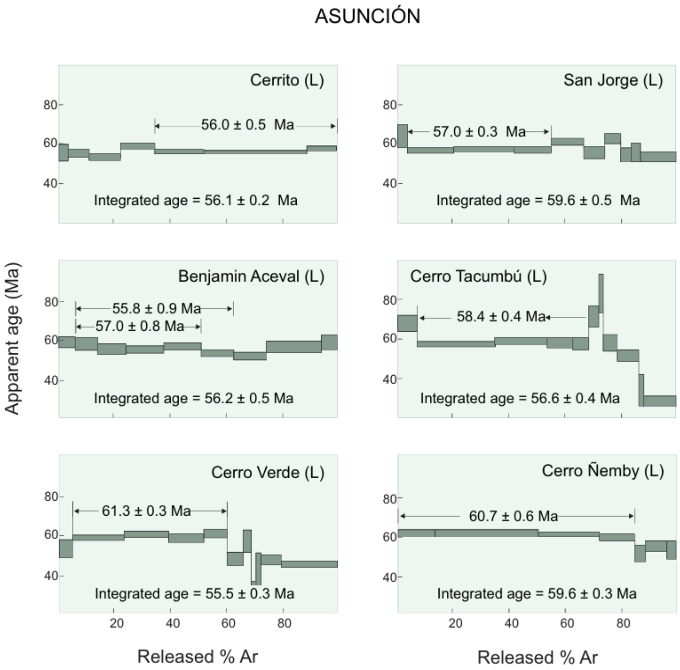

Figure 5. Ar/Ar spectra for volcanic rocks from the Asunción province (after MILAN, 2003; COMIN-CHIARAMONTI *et al.,* 2007c).

2.5 PERIODICITY OF THE MAGMATISM

The recurrence of alkaline magmatism affecting the Paraná Basin, as evidenced by successive episodes spanning 200 Ma, has motivated researchers to investigate its possible causes. A tectonic model was proposed by SADOWSKI (1987), in which generation and emplacement of alkaline bodies were controlled by reactivation events at intervals of 20 to 25 Ma. By analyzing selected K/Ar histograms from numerous widespread occurrences (Ponta Grossa arch, Rio de Janeiro–São Paulo coastal belt, Rio de Janeiro–Minas Gerais transverse belt, Minas Gerais–Goiás belt, and Eastern Paraguay), ULBRICH *et al.* (1990) distinguished peaks of more intense magmatic activity. However, their study does not consider Middle Triassic (Alto Paraguay) and Paleogene (Asunción) alkaline rocks. The authors referred to these time intervals as *chronogroups*, which they associated with significant geological features. Using only data that met specific analytical requirements, along with averages for individual massifs (peaks of maximum alkaline activity) chronogroups were defined at 133 Ma, 108 Ma, 84 Ma, and 70–62 Ma as characteristic of major alkaline magmatic intensity. The 133 Ma and 84 Ma chronogroups are well evidenced in the histograms by ULBRICH and GOMES (1981) and THOMPSON *et al.* (1988), with values falling within 140-130 Ma and 90-80 Ma as dominant classes, respectively. The 108 Ma chronogroup was recently confirmed by GOMES *et al*. (2018b) with new radiometric ages for the massifs of Banhadão and Itapirapuã. The 70–62 Ma chronogroup represents an extension of Late Cretaceous magmatism into the Paleogene, as indicated by numerous Ar/Ar ages published in the literature over the past decades. Reliable analyses using modern and adequate methods are necessary to better define interruption and repetition ages, particularly in Eastern Paraguay, where analytical data suggests a narrow span of Early Cretaceous events. Despite the limitations and lack of confidence in many results, the alkaline magmatism seems to have experimented periods of inactivity and activity in response to tectonic processes.

3 GEOCHEMISTRY

3.1 MAJOR AND TRACE ELEMENTS

Alkaline magmatism is marked by a wide range of chemical compositions, from ultrabasic to acidic rock types. Felsic rocks—mainly including silica-undersaturated, saturated, and oversaturated types (nepheline syenites, syenites, quartz syenites, and granites)—are prevalent in the complexes of most provinces. These felsic rocks form intrusive bodies of various sizes, along with fine-grained equivalents occurring as dikes and volcanic rocks. In a few cases, significant differences in the silica content of felsic rocks can be observed within the same complex, as exemplified by the coexistence of silica-undersaturated (nepheline syenites) and silica-oversaturated (quartz syenites and granites) rocks in Itatiaia (BROTZU *et al.,* 1997), Cerro Siete Cabezas in Paraguay (COMIN-CHIARAMONTI *et al.,* 2005a), and Velasco in Bolivia (FLETCHER and BEDDOE-STEPHENS, 1987), for instance. The Central and Amambay provinces in Paraguay, along with the Ponta Grossa Arch, Alto Paranaiba, and Goiás provinces in Brazil, are notable for the significant occurrence of ultrabasic to basic rocks associated with carbonatites and related lithologies, including cumulate members of the ijolite series, phoscorites, bebedourites, and fenites. Three distinctive groups of rocks—kamafugites (madupites, katungites, and ugandites), kimberlites, and glimmerites—are potassic to ultrapotassic, mafic to ultramafic, and strongly silica-undersaturated in composition. These rocks are found almost exclusively in the Alto Paranaíba and Iporá–Rio Verde regions of Central Brazil. However, kimberlites are also reported in other Brazilian regions, such as Lages in the state of Santa Catarina, in Paraná, and as isolated intrusions within the Sul-Riograndense shield. Glimmerites, in turn, are identified in the complexes of Anitápolis, Araxá, Ipanema, and especially Catalão, where micaceous material (vermiculite) has been economically exploited for many years. An ultrasodic rock association characterizes the nephelinites and ankaratrites of the Asunción and Misiones provinces in Paraguay, where both rock types contain mantle xenoliths reaching up to 45 cm in size. The clasts are composed of spinel lherzolite, harzburgite, and dunite, along with irregular amounts of vitreous material. Crustal xenoliths—fragments of sedimentary, igneous, and metamorphic origin and varying in size—are also present.

Chemical data indicate that alkaline magmatism is predominantly composed of evolved silicate rocks—nepheline syenites, syenites, and quartz syenites—along with their fine-grained equivalents. In contrast, primitive ultramafic rock types (excluding the aforementioned lithologies) are relatively scarce, mainly represented by lamprophyric dikes occurring in a few complexes, such as Juquiá, Lages, and Piratini, as well as along the Mantiqueira range and the southern coast of Brazil. Effusive rocks are of relevance only in specific intrusions, notably those in Alto Paranaíba and Iporá-Rio Verde (Minas Gerais and Goiás), Piratini, Sapucaí, and especially in the massifs of Poços de Caldas and Tinguá.

Alkali relationships indicate that magmatism is predominantly potassic in composition, with considerable variability in the K/Na ratio. Sodic rocks are subordinate, described in both Brazilian and Paraguayan occurrences. Along the western margin of the Paraná Basin, they are found in the Alto Paraguay complexes, several bodies of the Central province, and in the Asunción and Misiones volcanic associations (GOMES *et al.*, 2023). In Brazilian domains, particularly in the central-eastern part of the basin, sodic rocks are typical of the Poços de Caldas and Bom Repouso massifs, occurring in smaller amounts in Itapirapuã, Itatiaia, Lages, Passa Quatro, the coastal islands of Búzios and Monte de Trigo (GOMES *et al.*, 2021), and the Tunas massif (GOMES *et al*., 1987). In most cases, these rocks form small, irregular zones rather than discrete bodies, except for the small dikes. Occasionally, however, they can occur in substantial volumes, as in Poços de Caldas (ULBRICH *et al*., 2005).

The coexistence of potassic and sodic rocks within the same massif or province is well-documented in the Sapucai district in central-eastern Paraguay, where two potassic evolutive series (AB-T, alkali basalt to trachyte; B-P, basanite to phonolite) are clearly characterized. There, sodic rocks are represented by hypabyssal (dikes) and volcanic types (plugs, lava domes), the former occurring either single or as part of the Sapucai dike-swarm, which is an expressive geological feature grouping more than 200 bodies (GOMES *et al.,* 1989; VELÁZQUEZ *et al.*, 2011; COMIN-CHIARAMONTI *et al*., 1992).

The distribution of mantle-normalized incompatible elements in evolved rocks (syenites and peralkaline phonolites) reveals strong enrichment in large-ion lithophile elements (LILE) and depletion in high-field-strength elements (HFSE). A conspicuous geochemical pattern emerges, marked by pronounced negative anomalies in Ba, Sr, P, and Ti, along with positive anomalies in Nb-Ta and Hf-Zr. This conforms well to the general trend identified by MORBIDELLI *et al.* (1995) for more differentiated alkaline lithotypes from southern Brazil. These features are clearly illustrated in diagrams for the three major massifs of the Serra do Mar province (Figure 6). In Paraguayan lithotypes, a distinct contrast in Nb-Ta behavior is observed between potassic and sodic varieties (Figure 7; COMIN-CHIARAMONTI *et al*., 1997). Potassic rocks, like the associated Early Cretaceous tholeiitic lavas of the Serra Geral group—both high- and low-Ti types—exhibit negative Nb-Ta anomalies, in contrast to the positive pattern typical of sodic rocks. Tholeiitic lavas are also characterized by low overall elemental abundances and a slight enrichment in LILE. Dikes and plugs from the Ponta Grossa province typically display the same geochemical signature as syenitic rocks, with pronounced negative anomalies in Ba, P, Ti, and, to a lesser extent, Sm and Y, alongside positive peaks in Nb and Zr (GOMES *et al.,* 2011b).

The chondrite-normalized rare earth element behavior of the alkaline syenitic rocks studied derives from high concentrations of REE and LREE/HREE enrichment, with variable degrees of $(La/Yb)_N$ fractionation, as mostly detected in numerous complexes across various provinces: Alto Paraguay (COMIN-CHIARAMONTI *et al.,* 2005a), all stocks from Velasco (Figure 8, cf. COMIN-CHIARAMONTI *et al*., 2005b), intrusions and dikes from Valle Chico (RUBERTI *et al*., 2005), phonolitic rocks from Piratini (BARBIERI *et al.,* 1987), major massifs from Serra do Mar, and bodies associated with the Cabo Frio Lineament (BENNIO *et al*., 2001; BROTZU *et al*., 2007). Also characteristic of these rocks is the concave-upward behavior of heavy elements, with a steady increase from Dy to LREE. Other patterns are also observed, such as a strong increase from Lu to La; flat HREE trends with a relatively weak decrease from La to Lu and MREE/HREE fractionation. Eu anomalies are frequent, suggesting accumulation or fractionation of alkali feldspar. Notably, the pattern for agpaitic rocks is like that of typical syenitic and granitic lithotypes.

The normalized-incompatible elements pattern observed in rocks of the mafic-ultramafic suite of southern Brazil (Ponta Grossa Arch and Serra do Mar provinces), usually representing different types of cumulates, exhibits variable I.E. ranges reflecting the modal mineralogy. A similar pattern is noticed in the Juquiá, Pariquera-Açu and Tunas complexes, characterized by a gentle and continuous increase in the concentration of incompatible elements from Yb to Rb. Enrichment in LILE elements is indicated in spidergrams of specimens from Ipanema and Jacupiranga (GOMES *et al*., 2011b), Ponte Nova (AZZONE, 2008), and the coastal island Monte de Trigo (ENRICH, 2005). Differences in more evolved syenitic rocks consist mainly of positive K and P spikes in Ipanema, particularly in glimmerites; a negative anomaly for Nb in melteigites from Jacupiranga; and positive anomalies for Ba and Nb-Ta in Monte de Trigo.

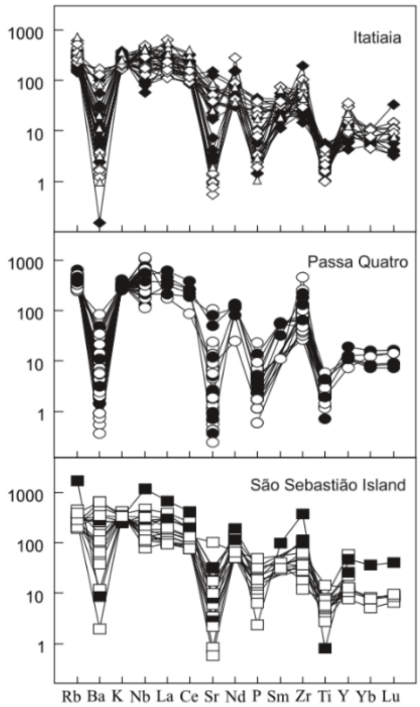

Figure 6. Diagrams of incompatible elements normalized to the primordial mantle (cf. MCDONOUGH and SUN, 1995) for the alkaline syenitic massifs of Itatiaia, Passa Quatro and São Sebastião island (after ENRICH *et al.,* 2005. simplified).

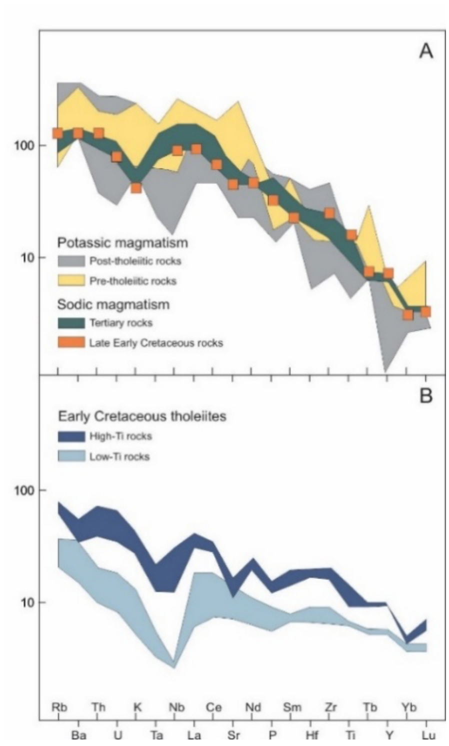

Figure 7. Trace-element data normalized to primitive mantle (cf. MCDONOUGH and SUN, 1995) for Eastern Paraguay: (A) potassic and sodic alkaline rocks, and (B) High- and low-Ti tholeiitic lavas (after COMIN-CHIARAMONTI *et al.*, 1997).

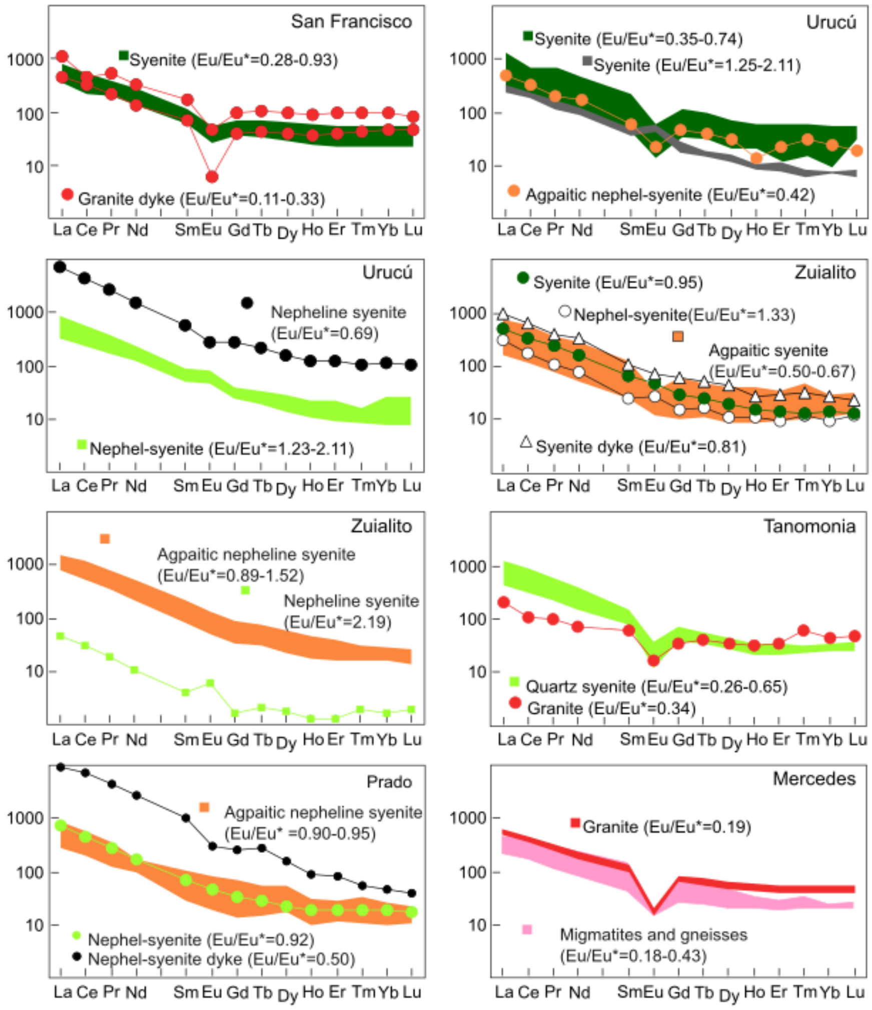

Figure 8. Chondrite-normalized REE distribution (cf. BOYNTON, 1984) for syenitic-granitic stocks from the Velasco province (after COMIN-CHIARAMONTI *et al.,* 2005b, simplified).

Data made available by GOMES and COMIN-CHIARAMONTI (2005) and BROD et al. (2005) for mafic-ultramafic lavas, dikes, and intrusions of peridotitic, kimberlitic and kamafugitic composition of various occurrences from the Alto Paranaíba and Goiás provinces exhibit different behaviors, usually characterized by large ion lithophile element enrichment and high field strength element depletion. For Alto Paranaíba rocks, negative anomalies in K, P, and Ti and occasionally in Rb, Sr, and Sm are common, whereas positive peaks are associated with Ba, La-Ce and Zr-Hf. Multi-element diagrams for the Goiás kamafugites display progressive enrichment in incompatible elements, with a peak at Nb-La-Ce and small anomalies in K, Rb, Sr, and, less obviously, P.

The behavior of rare earth elements (REE) in ultramafic and mafic rocks is mainly characterized by light-to-heavy REE (LREE/HREE) fractionation and the presence of parallel trends, as observed in alkaline stocks from the Central province in Paraguay (COMIN-CHIARAMONTI *et al.*, 1966), in complexes from the Ponta Grossa Arch—such as Pariquera-Açu (MORBIDELLI *et al.*, 2000), Ponte Nova (AZZONE, 2008), and Tunas (GOMES *et al.*, 1987)—and in several occurrences in northern Goiás (BROD *et al.*, 2005). A very uniform pattern, indicating strong enrichment in LREE relative to HREE, is reported by the last authors for the kamafugite series cropping out in the Goiás province. There, the rock types widely overlap, with katungites and mafurites being enriched in all rare earth elements (REE) relative to average leucite mafurites and ugandites. The latter types, in turn, show a much broader range of absolute REE concentrations. A similar behavior is suggested for the REE distribution in mafic-ultramafic rocks from the Alto Paranaiba province. Strong LREE/HREE fractionation is typical for intrusives and lavas. Negative anomalies Eu/Eu* are present in kimberlites, peridotites and kamafugitic dikes, whereas positive spikes have been observed in some types (GOMES; COMIN-CHIARAMONTI, 2005).

Carbonatites differ considerably from silicate rocks by their higher contents of incompatible and rare earth elements, with several complexes showing large compositional variability in terms of abundance, mainly due to the heterogeneous distribution and concentration of accessory mineral phases such as phosphates (apatite, monazite), oxides (pyrochlore, zirconolite), REE carbonates, and fluorocarbonates (ancylite, parisite). The stage of evolution also marks compositional differences among the rocks. Despite the pronounced scatter of incompatible and rare earth elements within individual complexes—particularly among samples representing different evolutionary stages (magmatic, late-magmatic, and hydrothermal)—carbonatites consistently exhibit a geochemical pattern of negative anomalies in K, Hf-Zr, Ti, and occasionally P, along with positive spikes in Th-U, La-Ce, and Ba (MORBIDELLI *et al*., 1995; COMIN-CHIARAMONTI *et al*., 2007a).

No significant differences in compositional patterns were noted by SPEZIALE *et al.* (2020a) among Early Cretaceous and Late Cretaceous carbonatitic complexes nor between magmatic and hydrothermal carbonatites or in occurrences with unusual geometric relationships. Nonetheless, complexes from the two main areas of carbonatite occurrences in Brazil - the Ponta Grossa Arch and the Alto Paranaiba-Goiás provinces - exhibit similar geochemical behaviors. In general, late-stage carbonatites are more enriched in nearly all elements than their early-stage counterparts.

Rare-earth elements display remarkable compositional scatters in the carbonatitic rocks, particularly in samples belonging to distinct stages of crystallization. The scatters may be due, at least partially, to the presence of accessory minerals, as observed in the distribution of incompatible elements. Patterns for Early and Late Cretaceous carbonatites (Figure 9) display a regular and strong decrease from La to Lu, mostly parallel to that of the associated apatite, suggesting that this mineral constrains the whole REE abundances in carbonatites. In the Mato Preto and Lages, behaviors are controlled by fluorite in the first case and by late carbonatite veins bearing barite and fluorocarbonates in the second. Additional distribution patterns are a flat LREE with a relatively weak decrease from La to Lu, a concave one with an HREE plateau, and a steady decrease from LREE to Dy (COMIN-CHIARAMONTI *et al*., 2005c). A negative Eu anomaly, also present in the coexisting apatite, is noticed in the Cerro Chiriguelo and Cerro Sarambí complexes in Paaguay.

3.2 C-O ISOTOPES

Data on stable oxygen and carbon isotopic ratios in carbonates of carbonatitic rocks from the southern Brazilian Platform are available from several studies (e.g., CENSI *et al*., 1989; MORIKIYO *et al*., 1990; SANTOS *et al*., 1990; SANTOS and CLAYTON, 1995; COMIN-CHIARAMONTI *et al.,* 1996; CASTORINA *et al.,* 1996; SPEZIALE *et al*., 1997; GUARINO *et al.,* 2012, 2017) and are discussed in great detail by CASTORINA *et al.* (1997), COMIN-CHIARAMONTI *et al.* (2005c, d; 2007a), GOMIDE *et al.* (2016), GOMES and COMIN-CHIARAMONTI (2017), GOMES *et al.* (2018a) and SPEZIALE *et al.* (2020b).

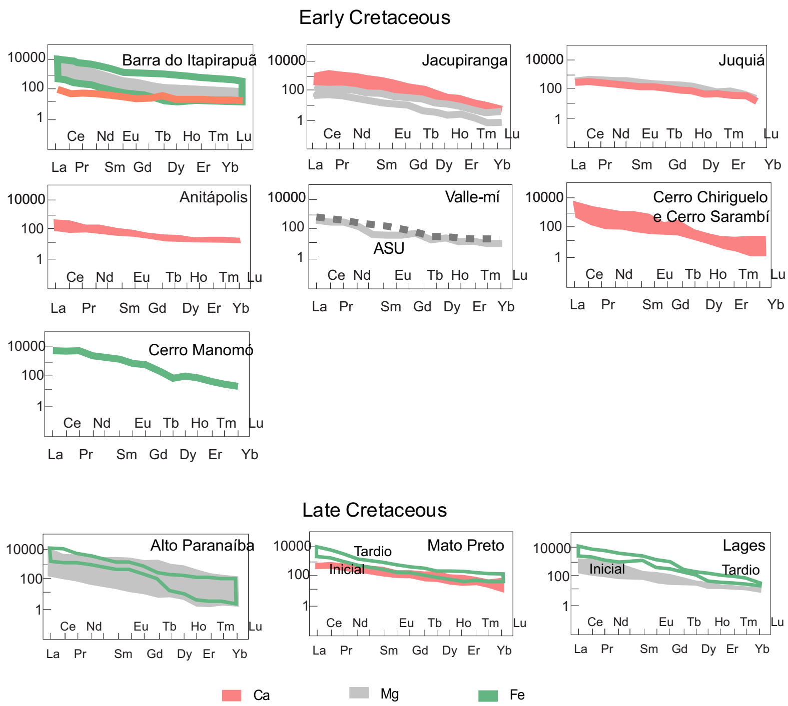

Figure 9. REE chondrite-normalized diagrams for Early to Late Cretaceous carbonatite complexes in the Brazilian Platform (after COMIN-CHIARAMONTI *et al*., 2005c). Ca, Mg and Fe carbonatites oldest to youngest, respectively.

Worldwide carbonatites show a wide range of δ^{18}O values, from about 5 to 25‰ vs. V-SMOW notation, but 50% of the analyses fall into a narrow interval of 6 and 10%. The variation of δ^{13}C‰ is more restricted, with 91% of the values between -2‰ and -8‰ vs. PDB-1 (DEINES, 1989). Ranges of δ^{18}O and δ^{13}C between 6 and 10‰ and between -4 and -8‰, respectively, represent the composition of primary carbonatites (TAYLOR *et al.,* 1967; KELLER; HOEFS, 1995). The differences in these parameters may be attributed to various reasons, such as (1) different emplacement levels of carbonatites, ranging from deep-seated up to near surface (DEINES and GOLD, 1973); (2) isotopic compositional differences in the source; (3) fractionation processes acting during the magmatic evolution; (4) loss of fluids during compression at the time of emplacement; (5) crustal contamination; and (6) post-magmatic and deuteric-groundwater processes. The latter processes are of local importance, yielding samples strongly enriched in light carbon due to biogenic contamination (CASTORINA *et al.,* 1997). Most of the variation in heavy oxygen in carbonatites from the Brazilian Platform could be explained by their interaction with hydrothermal fluids, whereas the variations in heavy carbon might be associated with both primary (i.e., isotopic composition of parental magma) or secondary (i.e., hydrothermal re-equilibration) processes (TAYLOR *et al*., 1967; PINEAU *et al*., 1973; DEINES, 1989).

Carbonates from distinct carbonatites (*magmatic*: Anitápolis, Araxá, Catalão I, Catalão II, Cerro Sarambí, Ipanema, Jacupiranga, Juquiá. Lages, Mato Preto, Tapira; *hydrothermal*: Barra do Itapirapuã, Cerro Chiriguelo; *unusual geometry*: Valle-mí) plotted in the δ^{13}C‰ (PDB-1) vs. δ^{18}O‰ (V-SMOW) diagrams of GOMES *et al.* (2018a) display trends that are indicative of variable behavior for the analyzed carbonate phases (calcite, dolomite, and ankerite). A mantellic composition is typical of the Jacupiranga carbonatites, with the isotopic values lying entirely within the carbonatite box (Figure 10), believed to represent a primary signature (HUANG *et al*., 1995). The large variations in heavy oxygen are likely due to the interaction with hydrothermal fluids, as well-illustrated by the Barra do Itapirapuã trend. Variations in heavy carbon isotopes appear to be associated with both primary and secondary processes (SPEZIALE *et al.*, 2020b), interpreted as resulting from mantle source heterogeneity (NELSON *et al.*, 1988) or crustal contamination by country rocks. SANTOS and CLAYTON (1995) report $\delta^{18}O$ values ranging from +11.5‰ to +14.0‰ and $\delta^{13}C$ values from -6.9‰ to +0.8‰ in Mato Preto carbonatites, attributed to contamination from adjacent limestones of the Açungui group. Additionally, changes are related to magmatic vs. hydrothermal evolution at shallow levels, as observed by Censi et al. (1989) for the Cerro Chiriguelo carbonatite in Paraguay. An isotopic evolution consistent with magmatic fractionation also characterizes early-stage carbonatites from the Alto Paranaiba province (GOMIDE *et al.*, 2016), whereas occurrences of later stages reveal magmatic fractionation combined with other genetical processes, such as percolation of carbohydrothermal fluids and hydrothermal alteration.

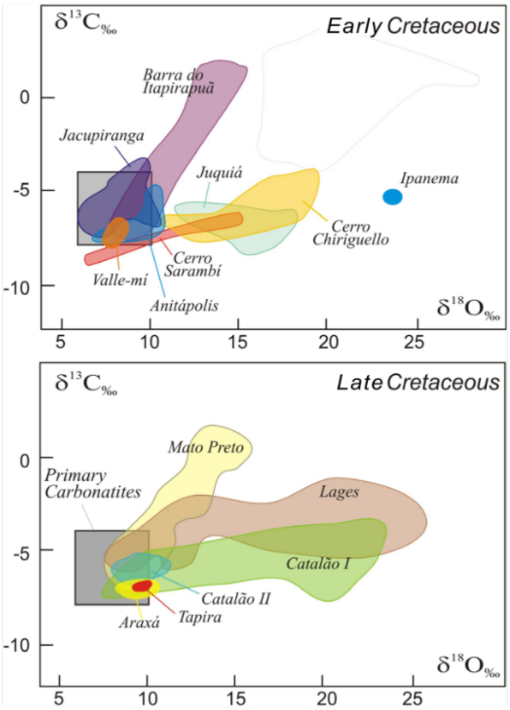

Figure 10. Fields of §13C‰ (PDB-1) and §18O‰ (V-SMOW) for Early Cretaceous (Brazil and Paraguay) and Late Cretaceous (Brazil) carbonatites (after GOMES *et al*., 2018a). Field for primary carbonatites box after TAYLOR *et al.* (1967) and KELLER; HOEFS (1995).

Systematic investigation of carbonatites of the Brazilian Platform indicates that most occurrences are isotopically enriched, showing no evidence of a particular crustal signature, while values for stable isotopes seem not to be strongly affected by fractional crystallization and liquid immiscibility processes (SANTOS; CLAYTON, 1995; CASTORINA *et al*., 1997; COMIN-CHIARAMONTI *et al.,* 2005c). SPEZIALE *et al.* (2020b) estimated the influence of both processes to represent no more than 2% of the values obtained, interpreting the main variations of $\delta^{18}O$ and $\delta^{13}C$ as due to isotopic exchange between the carbonatites and H_2O-CO_2-rich fluids at different temperatures (in the range of 400-80ºC) and variable CO_2/H_2O ratios in a hydrothermal environment (0.8 to 1).

A clear distinction can be drawn between Early Cretaceous (Ponta Grossa Arch province) and Late Cretaceous (Alto Paranaíba province, APIP) carbonatites. The former are in general associated with a potassic magmatism that shows, in accordance with FOLEY's classification (1992), "plagioleucitic" affinity (GOMES *et al*., 1996b), mainly represented by evolved rock types grouping syenites and fine-grained counterparts. The latter, on the other hand, are usually characterized by kamafugitic associations (GIBSON *et al*., 1995). In a similar way, GUARINO *et al.* (2017) distinguished two contrasting compositional terms in Brazilian carbonatites, ranging from Na-rich (olivine nephelinites, olivine melilitites, basanites), in the southernmost region of the country to nearly Na-free (ultrapotassic/kamafugitic) compositions in central areas (APIP). Less-evolved lithologies (gabbro-basalt clans) and cumulatic assemblages (e.g., dunite, clinopyroxenite, phoscorite) are common to complexes of both areas.

3.3 Sr-Nd-Pb ISOTOPES

Isotopic data from several alkaline complexes in the Brazilian Platform are present in a wide distribution, describing, in the conventional $(^{87}Sr/^{86}Sr)_i$ vs. $(^{143}Nd/^{144}Nd)_i$ diagram (Figure 11), a trend similar to the "Low Nd" array of HART and ZINDLER (1989). The distinction between potassic and sodic lithotypes is clearly evidenced based on isotopic values, with the former rocks, which pre- and post-date tholeiites of the Serra Geral group, associated with carbonatites and higher initial (time integrated) Sr and lower initial Nd with respect to the "Low Nd" array. Conversely, sodic rocks fall near the bulk-Earth composition and are mostly concentrated in the depleted quadrant. Sr and Nd are notably between potassic and sodic of composition rock types in the associated tholeiites (high and low Ti).

In alkaline rocks from Paraguay, including the Cerro Chiriguelo and Cerro Sarambí carbonatites, which outcrop with pre-tholeiitic potassic rocks, the initial $^{87}Sr/^{86}Sr$ (Sr_i) and $^{143}Nd/^{144}Nd$ (Nd_i) ratios range from 0.70636 to 0.70721 and from 0.51194 to 0.51165, respectively (COMIN-CHIARAMONTI *et al*., 2007c). These values are quite distinctive in respect to late Early Cretaceous sodic rocks from Misiones (ca. 118 Ma, Sr_i = 0.70435-0.70524, Nd_i = 0.51225-0.51242) and the Paleogene sodic rocks from Asunción (ca. 60 Ma, Sr_i = 0.70362-0.70392, Nd_i = 0.51259-0.51277), both plotting within the depleted quadrant towards the high U/Pb mantle (HIMU). Data for Middle Triassic sodic rocks from the Alto Paraguay province yielded Sr_i = 0.70350-0.70570 and Nd_i = 0.51123-0.51207 (GOMES *et al*., 2023), except for two samples of satellite stocks I and II from Cerro Siete Cabezas and one sample from a dike in Cerro Pedreira with higher Sr ratios. Similarly to the other sodic occurrences, these rocks fall within the depleted quadrant. Initial $^{87}Sr/^{86}Sr$ and $^{143}Nd/^{144}Nd$ ratios proposed by COMIN-CHIARAMONTI *et al.* (2007c) for the three sodic provinces are 0.703749 and 0.512390 (Alto Paraguay), 0.704157 and 0.512411 (Misiones), and 0.703596 and 0.512717 (Asunción), respectively.

Results for the Early Cretaceous potassic alkaline-carbonatitic complexes in Brazil (Sr_i = 0.70425-0.70595, average 0.70527 ± 0.00036) and Nd_i = 0.51213-0.51280, mean 0.51224 ± 0.00011) are also reported by Comin-Chiaramonti et al. (2007c). Whereas those relative to Late Cretaceous occurrences show the following mean values: Alto Paranaiba, Sr_i = 0.70527 ± 0.00036 and Nd_i = 0.51224 ± 0.00006 (BIZZI *et al*., 1994; GIBSON *et al*., 1995, and references therein); Taiúva-Cabo Frio and Serra do Mar, Sr_i = 0.70447 ± 0.00034 and Nd_i = 0.51252 ± 0.00008 (THOMPSON *et al*., 1998); Lages, Sr_i = 0.70485 ± 0.00053 and Nd_i = 051218 ± 0.00022 (COMIN-CHIARAMONTI *et al*., 2002).

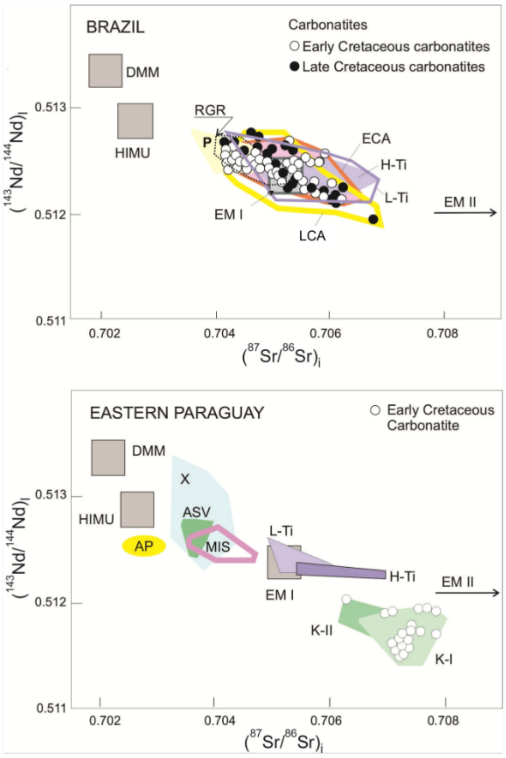

Figure 11. Initial $^{87}Sr/^{86}Sr$ (Sr_i) vs. $^{143}Nd/^{144}Nd$ (Nd_i) diagrams for magmatic rocks from Brazil and Eastern Paraguay (after COMIN-CHIARAMONTI *et al*., 2005c, 2007c, modified). Legends: H-Ti and L-Ti, Early Cretaceous flood tholeiites high and low in TiO_2, respectively; ECA and LCA, Early and Late Cretaceous alkaline rocks, respectively; P, Paleogene alkaline rocks from the Serra do Mar Range; K-I and K-II, Early Cretaceous potassic alkaline rocks, pre- and post-tholeiites; AP, Alto Paraguay Middle Triassic sodic alkaline rocks; MIS, late Early Cretaceous sodic alkaline rocks; ASU, Paleogene sodic alkaline rocks from the Asunción province and associated mantle xenoliths (x); fields for DMM, HIMU, EM I, and EM II after ZINDLER and HART (1989).

Data on Pb isotopes are relatively scarce, most of which are available from a few studies on late Early Cretaceous (Misiones province) and Paleogene (Asunción province) alkaline rocks in Paraguay (ANTONINI *et al*., 2005; VELÁZQUEZ *et al*., 2006) and some alkaline-carbonatitic occurrences in Brazil (COMIN-CHIARAMONTI *et al*., 2005c, 2007a; BIZZI; ARAÚJO, 2005; BECCALUVA *et al*., 2017; GOMES; COMIN-CHIARAMONTI, 2017). Following ZINDLER and HART (1986), Pb results may be used to discriminate between DMM and HIMU mantle components. The initial Pb isotopic compositions of both pre- and post-tholeiitic K-magmatism from Paraguay for most "primitive" rock types show $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$ values of 16.888-17.702, 15.433-15.620 and 37.156-37.915, respectively. With a few exceptions, these values are generally consistent with the Brazilian equivalents reported by MARQUES *et al.* (1999). Ratios for the Brazilian Late Cretaceous occurrences (Alto Paranaiba province) vary within narrow intervals of 17.51-18.52, 15.44-15.55 and 38,20-38.76, respectively. In contrast, the Paraguayan alkaline sodic lithologies differ from potassic rock-types, showing $^{206}Pb/^{204}Pb$ = 18.211, $^{207}Pb/^{204}Pb$ = 15.628 and $^{208}Pb/^{204}Pb$ = 37.063 (Misiones province) and $^{206}Pb/^{204}Pb$ = 18.964, $^{207}Pb/^{204}Pb$ = 15.678 and $^{208}Pb/^{204}Pb$ = 38.484 (Asunción province). In the $^{87}Sr/^{86}Sr$ vs. $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$, and $^{208}Pb/^{204}Pb$ diagrams of ANTONINI *et al.* (2005), the available data plot between the EMI and HIMU components, with the Paleogene sodic rocks from Asunción showing a shift toward the HIMU field. These authors interpret the Sr-Nd-Pb isotopic data as indicative of two distinct mantle sources responsible for the Cretaceous to Paleogene alkaline magmatism: (a) an extreme and heterogeneous EMI component, predominant in Cretaceous potassic events; and (b) a HIMU component, more influential in Cretaceous and Paleogene sodic events.

Focusing specifically on the Early Cretaceous Jacupiranga carbonatite complex, BECCALUVA *et al.* (2017) reported variable Pb isotopic compositions for petrographic associations that are common to several intrusions. The northwest Jacupiranga body includes alkali gabbros, syenodiorites, and syenites around dunites, whereas the southeast intrusion consists of clinopyroxenites, rocks of the melteigite-ijolite-urtite series, and associated carbonatites. Values for $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$ ratios of the first association range from 17.34 to 17.94, from 15.49 to 15.59, and from 37.94 to 38.93, respectively. The second association shows ratios of 17.70 to 17.87, 15.47 to 15.50, and 38.03 to 38.41, respectively. Isotopic ratios for the carbonatitic rocks are 17.21, 15.42, and 37.87, respectively. According to these authors, the silicate and carbonatitic rocks are significantly different in Sr-Nd-Pb isotopic composition, indicating an origin from parental magmas derived from independent mantle sources.

Alkaline magmatism affecting the Brazilian Platform spans approximately 200 million years, from the Middle Triassic to the Paleogene. Except for Paleogene sodic volcanic rocks exposed near Asunción, Paraguay, the older lithotypes are predominantly concentrated along the western margins of the Paraná Basin. The overall spatial distribution of magmatic ages suggests a progressive decrease in age from west to east. Magmatic activity is marked by discrete peaks distributed across a broad area, displaying varied ages as well as diverse mineralogical, petrographic, and geochemical characteristics.

The genesis of the corresponding alkaline rocks is commonly attributed to prolonged fractional crystallization of magmas derived from a lithospheric mantle source at relatively shallow crustal levels, typically less than 5 km beneath the surface, and low degrees of partial melting (COMIN-CHIARAMONTI *et al.,* 1997, 2005; ENRICH, 2005; ULBRICH *et al.*, 2005; MELLUSO *et al.,* 2017; GOMES and COMIN-CHIARAMONTI, 2017; GUARINO *et al*., 2019). In more advanced stages of magmatic evolution, differentiated syenitic melts are generated through the removal of mafic mineral assemblages, which may crystallize locally or evolve further into more residual peralkaline liquids. Late-stage crystallization gives rise to residual magmatic liquids that are metasomatically enriched in H_2O, CO_2, F, REE-carbonates, and incompatible elements (I.E.), and may also lead to the formation of rare accessory minerals. COMIN-CHIARAMONTI *et al.* (1997) interpreted these alkaline rocks as originating from a small subcontinental mantle mass characterized by vertical and lateral heterogeneities in composition and variable enrichment in incompatible elements. Carbonatites associated with silicate rocks are formed through a variety of petrogenetic processes, primarily including extreme fractional crystallization, liquid immiscibility, and fenitization. In their geochemical investigation of the Alto Paranaiba carbonatites, GOMIDE *et al.* (2016) suggested that additional processes may have contributed to the evolution of these rocks, such as degassing and interaction with hydrothermal and carbohydrothermal systems, often occurring in recurrent events.

Parental magmas of silicate alkaline rocks are believed to be of basanitic composition—including ankaratritic and alkali basaltic types—as suggested by the frequent occurrence of such lithologies in the field. These are typically observed as small dikes cutting through other alkaline rock types in various localities, such as Búzios, Monte Trigo, and Vitória islands (GOMES *et al.,* 2017; ENRICH, 2005; MOTOKI *et al.,* 2018, respectively), Juquiá (BECCALUVA *et al*.,1992), and the Mantiqueira range within the Serra do Mar province (THOMPSON *et al*., 1988; BROTZU *et al.,* 2005; AZZONE *et al*., 2018), as well as Valle-mí (GIBSON *et al*., 1995). These magmas may also be emplaced into country rocks exposed near alkaline intrusions. Mass balance calculations carried out in some complexes (Piratini, for instance, cf. BARBIERI *et al*., 1987) based on major element distribution confirm that interpretation. A distinct set of parental magmas can be proposed for each locality based on the distribution of Sr and REE in eudialyte-group minerals (SCHILLING *et al*., 2011; ENRICH *et al*., 2016). Due to the plagioclase fractionation during magmatic evolution, low Sr content and pronounced negative Eu anomalies suggest an association between eudialyte-group minerals and basanitic parental magmas. Mineral data available from GOMES *et al.* (2023) support the interpretation of such a parental magma for the alkaline rocks of the Passa Quatro massif and the Búzios and Monte de Trigo coastal islands. In contrast, the Poços de Caldas complex exhibits distinct characteristics, such as a high Sr content in eudialyte-group minerals and the absence of pronounced Eu anomalies, features that suggest association with strongly silica-undersaturated magmas. The alkaline-carbonatitic occurrences in the Alto Paranaíba province are believed to representt a distinctt petrogenetic evolution . Studies performed on these rocks by OLIVEIRA (2015) and OLIVEIRA *et al.* (2017) showed an abundance of phlogopite picrite dikes within the complexes or in theirvicinity and primitive mineralogical and chemical compositions. These dikes bear immiscible carbonate globules that point to a strong association between them and the associated carbonatites (BROD *et al.,* 2000, 2013). Therefore, phogopite picrite is considered to represent the parental magma for the alkaline-carbonatitic associations from the Alto Paranaiba province, including Catalão I and Catalão II (GUARINO *et al.,* 2013), and the Salitre and Tapira complexes (OLIVEIRA *et al*., 2017).

Two similar but distinct parental magmas emerge for the alkaline rocks based on studies carried out in Paraguayan occurrences. A source characterized by strongly fractionated REE and negative Nb-Ta-Ti anomalies is proposed for the potassic rocks, whereas the sodic rock-types are distinguished by slight positive anomalies in Nb-Ta. Sr-Nd isotopic data confirm the distinction of potassic rocks, enriched in radiogenic Sr and low in radiogenic Nd, from the sodic rocks, close to bulk Earth, and transitional to the Paraná flood tholeiites.

Other processes (e.g., crustal contamination, mixing of different magma types, metasomatism) seem to have exerted some local influence on the genesis of the alkaline rocks. However not conspicuously significant for the generation of the whole alkaline magmatism, assimilation of crustal components caused by interactions between magma chambers and adjacent host rocks is suggested for several known occurrences, mainly based on high Sr radiogenic isotope and the presence of evolved silica-undersaturated (phonolites) and silica-oversaturated (quartz syenites and granites) rocks, as described in the following occurrences: Banhadão (Sr_i = 0.70657-0.70849, Nd_i = 0.51153-0.51227, in phonolite dikes, RUBERTI *et al.* 2012), Cananeia (Sr_i = 0.7065-0.7070 and 07054-0.7078, in less and more evolved syenitic rocks, respectively, SPINELLI and GOMES, 2009), Cerro Caá Jhovy-Estancia Ramirez (Sr_i = 0.70517-0.70523 and Nd_i = 0.51206-0.51226, in peralkaline phonolite dike, VELÁZQUEZ *et al*., 2006), Cerro Siete Cabezas satellite bodies, stocks I and II, and Cerro Pedreira dike (Sr_i = 0.70418-0.71602, 0.70374-0.70767 and 0.70571, respectively; Nd_i = 0.51216, GOMES *et al.,* 2023), Ipanema (Sr_i = 0.70655-0.71385, in rocks of variable composition, GUARINO *et al.,* 2012), Jacupiranga (Sr_i = 0.705835 and 0.706086, Nd_i = 0.511867 and 0;512009, respectively; CHYMZ *et al.,* 2017), Juquiá (Sr_i = 0.7060-0.7078, in dikes and border facies, BECCALUVA *et al*., 1992), Ponte Nova (AZZONE *et al*., 2016), Tunas (Sr_i = 0.70777-0.70806, in syenitic dikes, GOMES *et al*., 1987). Additionally, the presence of crustal assimilation has been mentioned for the carbonatite complexes of Salitre (OLIVEIRA, 2015), Lages (TRAVERSA *et al*., 1996), Tapira (BROD *et al*., 1999) and Catalão I (OLIVEIRA, 2015; OLIVEIRA *et al*., 2017) and a few intrusions associated with the Cabo Frio Lineament province (e.g., Cabo Frio, Rio Bonito, Tangá; cf. SICHEL et al., 2012).

T^{DM} (Nd) model ages available for alkaline and tholeiitic rocks and associated carbonatites from both southeastern Brazil and Paraguay (CASTORINA *et al*., 1997;

COMIN-CHIARAMONTI *et al.,* 1997, 2007b, c; CARLSON et al., 2007; GOMES *et al*., 2011b and others) allow distinct peaks of metasomatism events to be identified, which affected the alkaline magmatism in different regions of the Paraná Basin. Nd model ages for Early Cretaceous potassic pre-tholeiitic rocks in Paraguay involve two peaks, one at 1.1 Ga (Valle-mí region, Rio Apa province) and the other one at 1.4 Ga (Amambay province), respectively, while post-tholeiitic rock-types yield T^{DM} values varying from 0.6 to 0.9 Ga. Late Cretaceous alkaline rocks and carbonatites in Brazil (Alto Paranaiba province, -1.0-0.8 Ga; GIBSON et al. 1997) and late Early Cretaceous (Misiones province) and Paleogene (Asunción province) occurrences in Paraguay yield ages within the 0.6-1.0 Ga interval, with the youngest values associated with the Asunción province (COMIN-CHIARAMONTI *et al*., 2007a). Data on Paraná volcanic rocks indicate T^{DM} (Nd) ages ranging mainly from 0.5 to 2.1 Ga for Hi-Ti flood tholeiites and dikes, with a mean peak at 1.1±0.1 Ga. Values for L-Ti tholeiites range from 0.7 to 2.4 Ga, with a mean peak of 1.6±0.3 Ga (COMIN-CHIARAMONTI *et al*., 2014). The large variability of the T^{DM} (Nd) ages seems to result from different metasomatic events that took place from the Paleoproterozoic to the Neoproterozoic, which led to the formation of isotopically distinct tholeiitic and alkaline magmas following two main subcontinental mantle enrichment episodes, at 2.0-1.4 Ga and 1.0-0.5 Ga (CASTORINA *et al.,* 1997; COMIN-CHIARAMONTI *et al*., 1997). These metasomatic events, which are marked by strong chemical differences in Ti, LILE and HFSE concentrations in alkaline rocks and tholeiites, have been interpreted by the latter authors as precursors to tholeiitic and alkaline magmatism manifestations in the Paraná Basin. Similarly to the age of magmatism, the enriched isotopic signature of the Early Cretaceous alkaline magmatism decreases from W (Paraguay) to E (southeastern continental margin of Brazil). These results suggest that the magmatism from the Paraná-Angola-Namibia system is related to both large- and small-scale heterogeneous source mantle (COMIN-CHIARAMONTI *et al*., 2007c).

4 ACKNOWLEDGEMENTS

Acknowledgements are due to the Brazilian Fapesp, the Foundation for Research Support of the State of São Paulo (Proc. 2019/22084-8) for the financial support. They are also due to M. Acquaviva and T.M.C. Samara for their valuable help in the production of tables and figures.

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